Nanostructured functional materials
via self-organization in organic thin films –
what can we learn from synchrotron x-ray scattering?

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On the current forefront in materials science are nanostructured materials with tailored properties. Self-organization processes in block copolymers, surfactant systems, or supramolecular assemblies can be used, among others, to provide a matrix structured on the mesoscopic scale, which can then be further functionalized with nanoparticles, enzymes etc.. For device applications, such materials are often prepared as thin films. The interfacial interactions can create further preferential orientation in the material which may be exploited as well. Self-organization is an attractive bottom-up mechanism to organize materials on the nano-scale, since top-down methods, like electron-beam writing, are costly and cannot cover macroscopic areas on films within reasonable processing times.

In the following, two types of self-organization shall be distinguished: chemical and physical processes. Chemical self-organization works via specific bonding. Examples are hydrogen bonds like (-COOH – NH_2-), coordination chemistry (for instance - terpyridine – ligand – terpyridine-), and self-assembled monolayers such as thiols on gold. The latter class of systems is important for anchoring molecular assemblies on a substrate in a well-defined way. This general approach has been termed supramolecular chemistry and was inspired by building principles and self-organization processes in biology. Classic examples in molecular biology are the DNA base pairing, protein-enzyme coupling, or virus-antigen interaction. Recently some groups have started using such biological systems for building functional films.

A more elusive concept is physical self-organization. The important mechanisms are electrostatic interactions, as in colloids and polyelectrolytes, hydrophobic/hydrophilic interactions as in surfactants and Langmuir-Blodgett films, as well as general interface energy and entropy balances as in diblock copolymer films. All of these systems display a variety of well-defined morphologies. Often there is no clean-cut separation between the various mechanisms of self-organization, and different types of self-organization processes can be combined to build ever-more complicated structures.

A third consideration in preparing functional films is, how to combine structural and functional components. Often the functional component, be it nanoparticles or enzymes, does not self-organize by itself in the desired configuration. In such a case a block copolymer film with the desired morphology, for instance, could be used as a template or scaffold, if the functional component is preferentially absorbed in or attached to one of the blocks. Again, there is a manifold of possibilities.

If we are able to synthesize such beautiful structures, the question arises immediately, how well did the self-organization work? Have we created only short-range order, or induced an ordering throughout the film? Does the film have the required structure normal to the substrate surface? The answer, i.e. how to probe the statistical properties of the prepared structures, lies in applying scattering techniques. The method of choice has to be sensitive to the mesoscopic scale (several nm to several 100 nm) and

has to be surface sensitive. The first requirement points to small-angle scattering (SAXS), the other to employing grazing incidence. In the remainder it will be demonstrated, how grazing-incidence small-angle x-ray scattering (GISAXS) can be used to study self-organization in functional thin films.

GISAXS encompasses all the features of small-angle scattering, but in addition, also concepts from grazing-incidence diffraction (GID) and diffuse x-ray reflectivity (XR) need to be applied, in order to extract the full information from the scattering images: The scattering rods from GID or the diffuse thickness oscillation from an XR detector scan may be found in a GISAXS pattern. Further care has to be taken in the interpretation, as simple kinematic scattering theory as used in SAXS does not suffice to explain important aspects of a GISAXS intensity map. For scattering angles close to the critical angles of the materials, distorted-wave Born approximation will provide a suitable description. This way, both lateral and normal structure factors as well as form factors may be determined, from which information such as typical length scales, preferential orientation, and size distributions may be extracted.

Two examples based on block copolymers shall be presented as illustration: Block copolymers exhibit a variety of morphologies, from ordered spheres to cylinders and lamellae to bicontinuous structures. If a symmetric copolymer is spin-coated onto a substrate, the film may display a preferential orientation with lamellae either parallel or perpendicular to the surface. Important factors are the interface energies and entropies of the blocks with the substrate. For simple polystyrene-polybutadiene block copolymers we found that polymers with short chains (less than 300 monomers) formed parallel lamellae, whereas films consisting of long chains (more than 1200 monomers) formed perpendicular lamellae on silicon wafers covered with the native oxide [1,2].

The second example are nanocomposites, based on polystyrene-polyethylene oxide copolymers (PS-PEO) forming spherical micelles: A silica precursor dissolved readily in the PEO matrix, but not in the PS spheres. After calcination, a silica matrix with a monolayer of monodisperse holes remains. From GISAXS we could determine the size and the average spacing of the holes [3]. All data were obtained at CHESS beamline D1 using multilayer optics and a CCD camera as detector. Complementary results from AFM and scanning electron microscopy are in good agreement with the GISAXS data.

In summary, GISAXS is a versatile technique of studying thin functional films in a non-invasive way. Accurate statistically-averaged information of the internal film structure is obtained and density correlations both parallel and perpendicular to the substrate can be studied. Other assets of GISAXS are, that no special sample preparation is necessary, and that due to the relatively simple scattering geometry, samples can be studied in in-situ environments, such as solvent vapor or vacuum. Even real-time observations are possible in some cases [1], due to the relatively high scattering intensity of nano-sized objects.

[1] Smilgies et al., Synchrotron Radiation News 15 (5), pp. 35-41 (2002).
[2] Papadakis et al., Advances in Solid State Physics, Vol. 44 (Springer Verlag, Heidelberg, 2004) pp. 327-338.
[3] Du et al., Advanced Materials 16, 953-957 (2004).